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Research Article

Removal of Methylene Blue from Wastewater by Adsorption onto $ZnCl_2$ Activated Corn Husk Carbon Equilibrium Studies

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The removal of methylene blue by activated carbon of corn husk by $ZnCl_2$ activation ($CHAC_Z$) was investigated in the present study. Adsorption studies were performed by batch experiments. The effect of pH, initial dye concentration, adsorbent dose, the particle size of $CHAC_Z$, agitation speed, temperature, and contact time was explored. The equilibrium adsorption data were analyzed using two widely applied isotherms: Langmuir, Freundlich. Best fits were found to be Freundlich isotherm. Langmuir adsorption capacity (Q_m) in 298, 308, and 318 K is 462.96, 546.45, and 662.25 mgg^{-1}. The amount of R_L indicates that $CHAC_Z$ has a favorable adsorption. Maximum MB removal was observed at pH 4.0. The results indicate that $CHAC_Z$ is an efficient adsorbent for removing dye from wastewater.

1. Introduction

More than 10,000 dyes have been widely used in textile, paper, rubber, plastics, leather and cosmetic, pharmaceutical, and food industries [1]. The discharge of colored wastes into the receiving water bodies not only affects their aesthetic nature but also interferes with the transmission of sunlight and therefore reduces the photosynthetic activity [2]. As dyes are designed to resist breakdown with time, exposure to sunlight, water, soap, and oxidizing agent cannot be easily removed by conventional wastewater treatment processes due to their complex structure and synthetic origins [3]. Methylene blue (MB) is cationic dyes. MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [4]. Various conventional methods such as physical, chemical, and biological processes have been tried for the removal of dyes from aquatic media [5–7]. Adsorption is one of the physical-chemical methods, which is found to be the most simple and economical to remove the dyes from effluents [8]. The adsorption attempts have been made to find alternative low-cost adsorbents [9]. Activated carbon prepared from these wastes helps to solve the waste disposal problem. Agricultural wastes include orange peel [10], jute fiber [11], wheat shells [12], soy meal hull [13], rice husk [14], activated date pit [15], and bamboo dust [16]. Most of the activated carbons are produced by a two-stage process carbonization followed by activation. The first step is to enrich the carbon content and to create an initial porosity and the activation process helps in enhancing the pore structure. Basically, the activations are two different processes for the preparation of activated carbon: physical activation and chemical activation. Among the numerous dehydrating agents, zinc chloride in particular is the widely used chemical agent in the preparation of activated carbon. Knowledge of different variables during the activation process is very important in developing the porosity of carbon sought for a given application. Chemical activation by zinc chloride improves the pore development in the carbon structure, and because of the effect of chemicals, the yields of carbon are usually high [17, 18]. In the present study, activated carbons prepared from husk corn have been used as an adsorbent for dye removal of MB. The effects of operating parameters such as initial dye concentration, adsorbent dosage, pH, agitation speed, contact time, particle size, and temperature were studied.

2. Materials and Methods

The raw material, husk corn, was repeatedly washed with distilled water to remove dirt, dust, and other impurities. The husk corn was dried 24 hours in oven with 383 K and then crushed and garbled. This material was impregnated with concentrated solution of husk corn powder to $ZnCl_2$ with ratio 1 : 1 in the mixed system and then dried in the oven at 383 K. The activation of the samples was performed in the furnace at 723 K for 5 h, washed thoroughly with distilled water until it attained the neutral pH, and soaked in KOH solution overnight in order to remove any excess alkali present. The material was then washed with distilled water until it reached neutral pH and dried at 723 K. A stock solution (1000 mg L^{-1}) of MB was prepared by dissolving an appropriate amount of each dye in double distilled water, which was diluted to desired batch adsorption experiments that were carried out to investigate the effect of pH, adsorbent dose, initial dye concentration, contact time, particle size, agitation speed, and temperature on the adsorption of MB. The experiments were carried out in 100 mL conical flasks by mixing a preweighed amount of adsorbent with 50 mL of dye solution and the solution was agitated at 150 rpm on a stirrer at constant temperature, and after shaking the solution, the reaction mixtures were centrifuged and the filtrate was analyzed using spectrophotometer. The adsorption isotherm experiment was carried out in a thermostatic orbital shaker at a constant speed of 150 rpm at different temperatures (298, 308, and 318 K) by adding agitating 50 mL of dye solution of various concentrations. After agitation, the dye solutions were separated from the adsorbent by centrifugation for 10 min. The dye removal was determined by a spectrophotometer using 665 nm as the maximum absorbance wavelength. The percentage removal of dye and the amount of dye adsorbed on adsorbent (q_e) were calculated, respectively, as follows:

$$\%\text{Removal} = \left(\frac{C_o - C_e}{C_o}\right) \times 100, \quad (1)$$

$$q_e = \left(\frac{C_o - C_e}{M}\right) V, \quad (2)$$

where q_e is the amount of dye adsorbed on adsorbent at equilibrium (mg g^{-1}), C_0 and C_e are the initial and equilibrium of dye concentration (mg L^{-1}) in solution, respectively, V is the volume of solution (L), and M is the weight of adsorbent (g).

3. Results and Discussion

3.1. Effect of pH. The pH of the dye solution plays an important role in the whole adsorption process, particularly on adsorption capacity [19]. Figure 1 shows the effect of pH on the adsorption of MB onto the $CHAC_Z$ at initial concentration of 50 mgL^{-1} MB and the amount of adsorbent (0.4 gL^{-1}) at 150 rpm agitation speed and at 298 K. If the pH of the dye solution was changed from 3 to 11, the adsorption capacity of $CHAC_Z$ was raised from 120.08 to 121.52 mgg^{-1}. In the process of adsorption, at a lower pH, the adsorbent surface is positively charged, favoring adsorption of anionic contaminants. Because MB is a cationic dye, positive charge which occupied the feasible adsorption position competes with dye molecules, resulting in a lower adsorption of dyes; while at a higher pH, negatively charged surface facilitates adsorption of cationic contaminants [20].

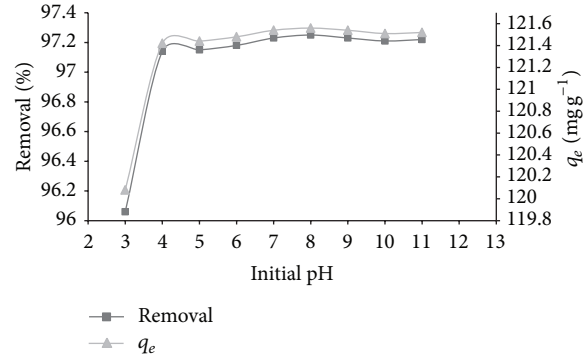

Figure 1: Effect of pH (C_o = 50 mgL^{-1}, adsorbent dose = 0.4 gL^{-1}, t = 120 min, A.S. = 150 rpm, T = 298 K).

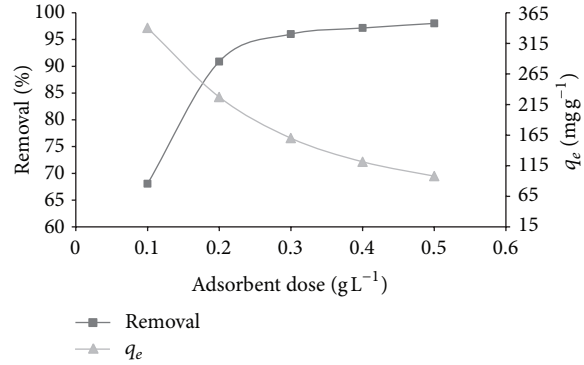

Figure 2: Effect of adsorbent dose (pH = 4, C_o = 50 mgL^{-1}, t = 120 min, A.S. = 150 rpm, T = 298 K).

3.2. Effect of Adsorbent Dose. This effect was studied using a dose of $CHAC_Z$ from 0.1 to 0.5 gL^{-1} that was shown in Figure 2. The results show that the percentage of adsorption was increased by increasing the dose of $CHAC_Z$ until 0.3 gL^{-1}. It is apparent that by increasing the dose of the $CHAC_Z$, the number of sorption sites available for sorbent-biosolute interaction is increased, thereby resulting in the increased percentage of MB removal from the solution. The decrease in sorbent capacity, that is, the amount of MB sorbed per unit weight of sorbent with increase in $CHAC_Z$ dose, may be attributed to two reasons. The increase in sorbent dose at constant MB concentration and volume will lead to unsaturation of sorption sites through the sorption process and secondly may be due to particulate interaction such as aggregation resulting from high sorbent dose. Such aggregation would lead to a decrease in total surface area of the sorbent and an increase in diffusional path length [21].

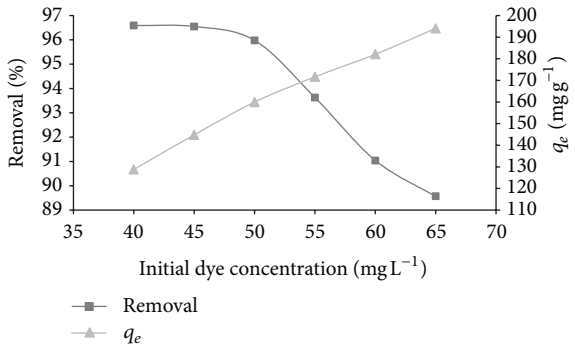

Figure 3: Effect of initial MB concentration (pH = 4, adsorbent dose = 0.3 gL^{-1}, t = 120 min, A.S. = 150 rpm, T = 298 K).

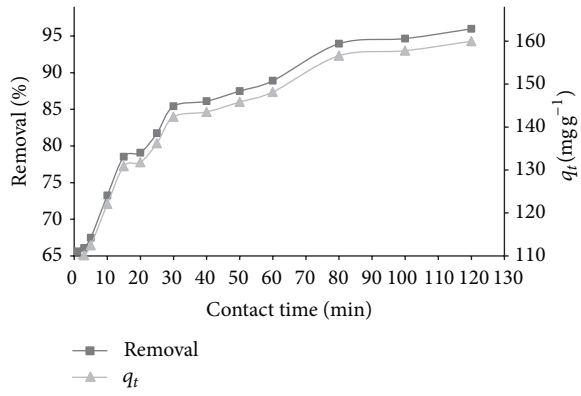

Figure 4: Effect of contact time (pH = 4, adsorbent dose = 0.3 gL^{-1}, C_o = 50 mL^{-1}, A.S. = 150 rpm, T = 298 K).

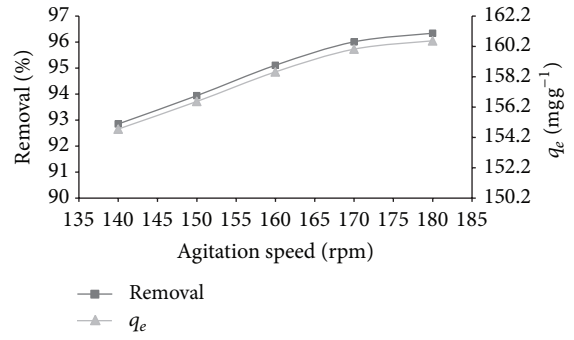

Figure 5: Effect of agitation speed (pH = 4, adsorbent dose = 0.3 gL^{-1}, C_o = 50 mgL^{-1}, t = 80 min, T = 298 K).

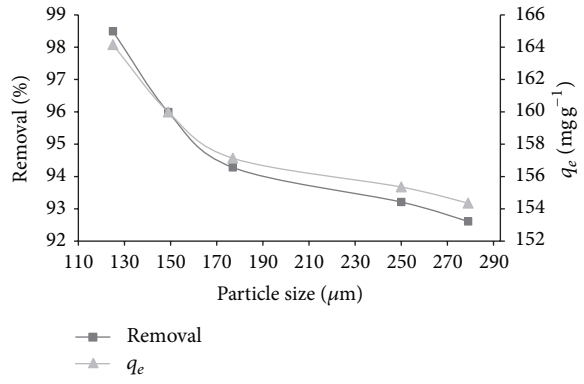

Figure 6: Effect of particle sizes (pH = 4, adsorbent dose = 0.3 gL^{-1}, C_o = 50 mgL^{-1}, t = 80 min, A.S. = 170 rpm, T = 298 K).

3.3. Effect of Initial MB Concentration. The effect of initial MB concentration (between 40 and 65 mgL^{-1}) on the adsorption of MB onto the $CHAC_Z$ was studied. The adsorption capacity of $CHAC_Z$ increased with increasing initial MB concentration and percent adsorption decreased with the increase in initial MB concentration, just as also shown in Figure 3. It means that the adsorption is highly dependent on initial concentration of MB. It is because of that, at lower concentration, the ratio of the initial number of MB molecules to the available surface area is low and subsequently the fractional adsorption become independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of MB is dependent upon initial concentration.

3.4. Effect of Contact Time. Contact time is also an important factor affecting removal; most of adsorption occurs in the initial half hour and increases very slowly later. These experiments have been carried out at variation of time of contact (0–120 minutes). Figure 4 shows that adsorption of MB onto the $CHAC_Z$ reached to the equilibrium in 80 minutes. It was reported that during adsorption of dyes, initially the MB molecules reach the boundary layer; then they have to diffuse into the adsorbent surface; and finally, they have to diffuse into the porous structure of the adsorbent. Therefore, this phenomenon will take a relatively longer contact time [22].

3.5. Effect of Agitation Speed. Agitation is an important parameter in adsorption phenomena influencing the distribution of the solute in the bulk solution and formation of the external boundary film. The effect of biosorption of MB onto $CHAC_Z$ was studied at different agitation speeds. The result is shown in Figure 5. It was observed that the adsorbed MB by $CHAC_Z$ increased with the increase in agitation speed. By further increasing the speed, there was a further increase in biosorption because all binding sites were available for further biosorption. With agitation, the external mass transfer coefficient increases resulting in quicker adsorption of the MB.

3.6. Effect of Particle Size. The effect of variation in particle size $CHAC_Z$ for an initial MB concentration of 50 mg^{-1} is shown in Figure 6. The experiments were carried out using $CHAC_Z$ with several particle sizes (125–279 μm). The results also showed that biosorption increases with an increase in particle size of biosorbents. The relatively higher adsorption with smaller adsorbent particle may be attributed to the fact that smaller particles yield large surface areas. The particle size decreases and surface area exposed to biosorption of MB increases as particle size increases. This may be due

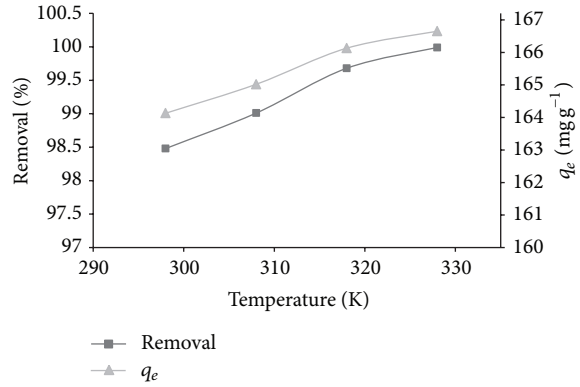

FIGURE 7: Effect of temperature (pH = 4, adsorbent dose = 0.3 gL^{-1}, C_o = 50 mgL^{-1}, t = 80 min, A.S. = 170 rpm).

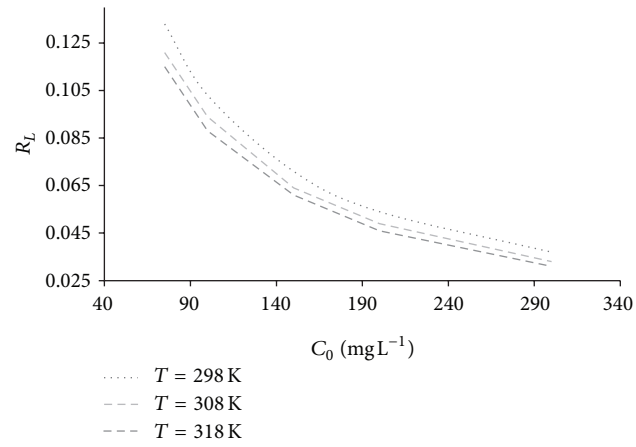

FIGURE 8: Comparison of R_L absorption of MB onto CHAC$_Z$ in three temperatures.

to an increase in the accessibility of the adsorbate to the pores of the biosorbents with the decrease in particle size. With biosorption being a surface phenomenon, the smaller biosorbent particle size offers comparatively larger surface area and higher biosorption occurs at equilibrium [23].

3.7. Effect of Temperature. This effect was investigated at (298–338 K). Figure 7 shows the adsorption capacity of CHAC$_Z$ increased from 164.13 to 166.65 mgg^{-1}, when the temperature was increased from 298 to 328 K. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [24].

3.8. Isotherm Studies. Equilibrium uptake of MB was investigated at 297 K with sorbent weight of 0.015 g of CHAC$_Z$ in contact with 50 mL of MB solutions and at pH 4.00. The flasks were shaken at 150 rpm and the equilibrium concentration of the remaining MB was determined spectrophotometrically. The equilibrium adsorption isotherm is of importance in the design of adsorption systems [25]. In general, the adsorption isotherm describes how adsorbents interact with adsorbents and thus is critical in optimizing the use of adsorbents. Several isotherm equations are available, and two important isotherms were selected for this study: the Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption [25].

The linearized Langmuir equation is represented as follows [26]:

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{1}{Q_m} C_e, \tag{3}$$

where b is the equilibrium constant or Langmuir constant related to the affinity of binding sites (Lmg^{-1}) or (Lmol^{-1}) and Q_m represents a partial limiting adsorption capacity when the surface is fully covered with MB molecules which assists in the comparison of adsorption performance. Q_m and b were calculated from the slope and interception of the straight lines of the plot C_{eq}/q_{eq} versus C_{eq} [27]. The Langmuir maximum adsorption capacity (Q_m) is 462.96, 546.45, and 662.25 mgg^{-1} at 298, 308, and 318 K, respectively.

Essential characteristics of the Langmuir isotherms can be described by a separation factor (R_L) which is defined by the following equation [28]:

$$R_L = \frac{1}{1 + b C_0}, \tag{4}$$

where C_0 is the initial concentration of MB (mgL^{-1}) and b is the Langmuir adsorption constant (Lmg^{-1}). The value of separation factor (R_L) indicates the nature of the absorption process [21]. In the absorption of MB onto CHAC$_Z$, (R_L)values were in the range of 0.063–0.080; this result shows that the absorption of MB onto CHAC$_Z$ is favorable. In Figure 8 the seen values of R_L absorption of MB onto CHAC$_Z$ decrease with increasing the temperature.

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems [26]. The Freundlich isotherm is given in logarithmic form as follows:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e, \tag{5}$$

where k_f and n are roughly an indication of the adsorption capacity of adsorbent and the adsorption intensity, respectively. k_f and (n) can be determined from the linear plot of log q_{eq} versus log C_{eq} [25]. k_f is a Freundlich constant that shows the strength of the relationship between adsorbate and adsorbent, and the values k_f of CHAC$_Z$ for MB adsorption are 114.55, 135.21, and 125.89 Lmg^{-1} at 298, 308, and 318 K, respectively. The n value of Freundlich equation could give an indication on the favorability of sorption. It is generally

Table 1: Langmuir and Freundlich constants for the adsorption of MB onto $CHAC_Z$.

T K	Langmuir				Freundlich		
	Q_m mg g^{-1}	b L mg^{-1}	r^2	R_L	k_f L mg^{-1}	n	r^2
298	462.96	0.087	0.995	0.080	114.55	3.47	0.996
308	546.45	0.097	0.958	0.072	135.21	3.41	0991
318	662.25	0.103	0.962	0.063	125.89	2.58	0.997

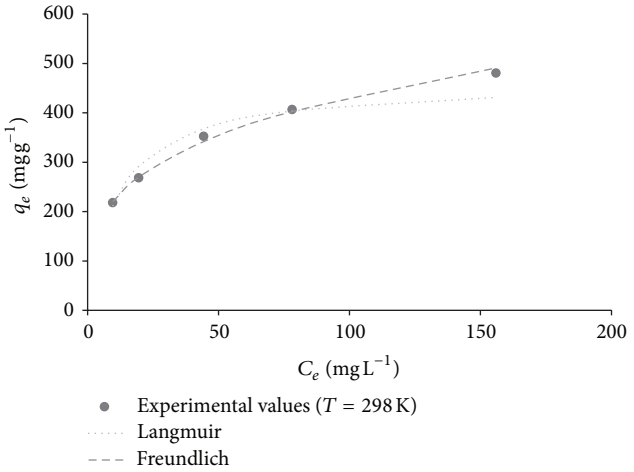

Figure 9: The Langmuir and Freundlich isotherms for the adsorption of MB onto $CHAC_Z$ (adsorbent dose: 0.3 gL^{-1}; pH: 4; temperature: 298 K).

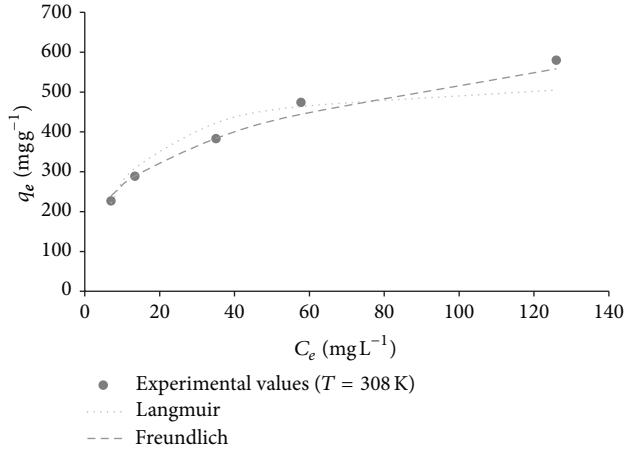

Figure 10: The Langmuir and Freundlich isotherms for the adsorption of MB onto $CHAC_Z$ (adsorbent dose: 0.3 gL^{-1}; pH: 4; temperature: 308 K).

stated that the values of n in the range of 1 to 10 represent good adsorption [27]. The values n of $CHAC_Z$ for MB adsorption were obtained between 1 and 10,and therefore this adsorption is favorable.

Figures 9, 10, and 11 show the plots comparing the Langmuir and Freundlich isotherms with the experimental

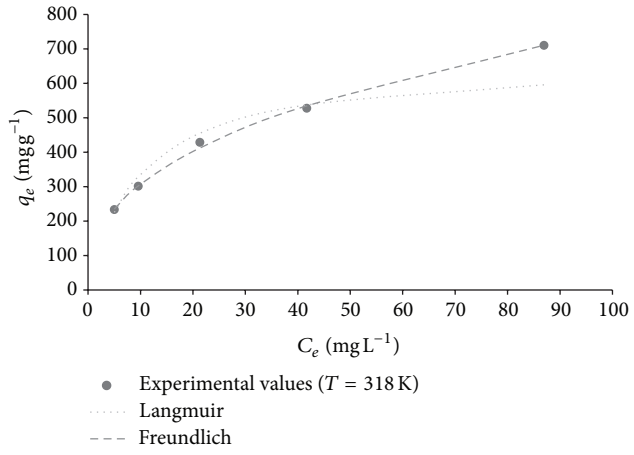

Figure 11: The Langmuir and Freundlich isotherms for the adsorption of MB onto $CHAC_Z$ (adsorbent dose: 0.3 gL^{-1}; pH: 4; temperature: 318 K).

data for the adsorption of MB onto $CHAC_Z$ at a pH of 4. The parameters and correlation coefficients obtained from the plots of Langmuir and Freundlich isotherms are listed in Table 1. By comparing the correlation coefficients obtained from the two isotherm models, the Freundlich isotherm gave the best correlation for the sorption process and adsorption of MB by the $CHAC_Z$ followed the Freundlich isotherm.

4. Conclusion

(i) $CHAC_Z$ can be used as an efficient and cheap absorbent for refining wastewater.

(ii) The amount of MB removed by $CHAC_Z$ increases with increasing these parameters: $SFAC_H$ dose, pH, contact time, agitation speed (rpm), and temperature, and thus, removal was increased by decreasing $CHAC_Z$ particle size, and initial MB concentration.

(iii) Adsorption behavior of the $CHAC_Z$ is described by Freundlich isotherm.

(iv) The amount of R_L showed that $CHAC_Z$ can be used for dye removal.

(v) Adsorption behavior is multilayer Freundlich type isotherms for the activated carbons.

(vi) The result indicates that $n > 1$; therefore this adsorption process is physical.

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